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NEW METHODS  
OF  
MEASURING  
THE  
SURFACE-TENSION  
OF LIQUIDS,

BY

*Thomas*  
T. PROCTOR HALL.

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Approved as a dissertation for the degree of Doctor of  
Philosophy in the Department of Physics at Clark University.

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NEW METHODS  
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I. HISTORICAL.

THE common way of measuring the surface-tension of liquids by finding the height to which they will rise in capillary tubes is simple and convenient, and is applicable to nearly all liquids. The degree of accuracy attainable is limited by (a) the narrowness of the tube, or else the shortness of the elevated liquid column, which limits the accuracy of measurement; by (b) irregularities in the bore of the tube; by (c) the difficulty in securing a clean surface, particularly in very small tubes; and by (d) impurities, such as dissolved air, in the body of the liquid. It is to the last two causes that most of the differences seen in the following table are probably due. The table gives the values of the surface-tension of water as found by various observers by means of capillary tubes. All values are given in dynes per centimetre, and the numbers in the second column are, where necessary, deduced by Brunner's formula for the relation of surface-tension to temperature.

## Surface-Tension of Water, by capillary tubes.

T.	T at 0° C.	Observer.	Reference.
74.4 at 0° C.	74.4	Artur.	<i>Théorie élémentaire de la capillarité.</i>
75.2 - 1405 f.	75.2	Brunner.	<i>Pogg. Ann.</i> lxx. p. 481 (1847).
74.0 at 8° 5.	75.2	Desain.	<i>Ann. Chim. Phys.</i> li. p. 383 (1857).
75.0 at 0°.	75.0	Frankenheim.	<i>Pogg. Ann.</i> xxxvii. p. 409 (1836).
75.4 - 141 f.	75.4	Frankenheim.	<i>Pogg. Ann.</i> lxxii. p. 177 (1847).
75.6 - 146 f.	75.6	Frankenheim & Sondhaus.	<i>Journ. Pr. Chem.</i> xxiii. p. 401 (1841).
74.2 at 8° 5.	75.4	} Gay-Lussac.	{ <i>Poisson, Nouvelle Théorie etc.</i> pp. 112, 181 (1831).
73.7 at 11°.	75.2		
73.1 at 10°.	74.5	Hagen.	<i>Pogg. Ann.</i> lxvii. pp. 1, 152 (1846).
77.1 - 179 f.	77.1	Jäger.	<i>Beibl.</i> xvi. p. 345 (1892); <i>Wiener Ber.</i> pp. 99 & 100 (1891).
71.0 at 19° 25.	73.7	Magie.	<i>Wied. Ann.</i> xxv. p. 432 (1885).
71.0 at 16° 2.	73.3	Quincke.	<i>Pogg. Ann.</i> cxxxix. p. 1 (1870); <i>Phil. Mag.</i> April 1871, p. 252.
72.1 betw. 15° & 20°.	?	Quincke.	<i>Pogg. Ann.</i> clx. p. 371 (1877).
71.8 at 17° 5.	74.3	Rodenback.	<i>Beibl.</i> iv. p. 105 (1880).
79.7 - 204 f.	79.7	Simon.	<i>Ann. Chim. Phys.</i> xxxii. p. 5 (1851).
75.4 - 144 f.	75.4	Sondhaus.	<i>Pogg. Ann.</i> Erg. viii. 1878, p. 266.
71.3 at 16° 2.	73.6	Volkman.	<i>Wied. Ann.</i> xi. p. 177 (1880).
75.8 - 143 f.	75.8	Volkman.	<i>Wied. Ann.</i> xvii. p. 361 (1882).
76.5 - 144 f.	76.5	Wolf.	<i>Pogg. Ann.</i> cii. p. 571 (1857).
77.3 - 1406 f.	77.3	Wolf.	<i>Ann. Chim. Phys.</i> xlix. p. 269 (1857).
54.9.	?	Wertheim.	<i>Pogg. Ann.</i> cii. p. 508 (1857).
Mean .....	75.4		

Capillary plates have been used by a few investigators in place of capillary tubes, with no apparent advantage. Volkmann\* found for water at 16° C.,  $T = 71.8$  dynes (74 at zero), while Wertheim† and Hagen‡ obtained values approaching 50 dynes.

Wertheim§ and Hagen|| obtained equally low values by measuring the capillary elevation of water at a single vertical plane wall. Quincke¶, neglecting the curvature in glass bottles 50 millim. in diameter, deduced from the capillary elevation of water in them  $T = 86.2$  dynes at zero. This method is obviously of no practical value.

In all of these three methods it is assumed that when the solid wall is wet by the liquid the angle of contact is zero. The validity of this assumption has been questioned by Quincke, who maintains\*\* the actual existence of a finite

\* *Wied. Ann.* xi. p. 177 (1880).

† *Pogg. Ann.* cii. p. 595 (1857).

‡ *Ibid.* cii. p. 595 (1857).

§ *Ibid.* lxxvii. p. 453 (1849).

|| *Ibid.* lxvii. pp. 1, 153 (1846).

¶ *Ibid.* cxxxv. p. 641 (1868), and *Phil. Mag.* August 1869, p. 95.

\*\* *Quincke*, *Wied. Ann.* xxvii. p. 219 (1886).



Reference.

*Éléments de la capillarité.*  
n. lxx, p. 481 (1847).  
n. *Phys.* li, p. 583 (1857).  
n. xxxvii, p. 409 (1836).  
n. lxxii, p. 177 (1847).  
n. *Chem.* xxiii, p. 401 (1841).  
  
*Nouvelle Théorie etc.* pp.  
81 (1831).  
n. lxxvii, pp. 1, 152 (1846).  
n. p. 345 (1892); *Wiener*  
99 & 100 (1891).  
n. xxv, p. 432 (1885).  
n. cxxxix, p. 1 (1870); *Phil.*  
April 1871, p. 252.  
n. clx, p. 371 (1877).  
n. p. 105 (1880).  
n. *Phys.* xxxii, p. 5 (1851).  
n. *Erg.* viii, 1873, p. 266.  
n. xi, p. 177 (1880).  
n. xvii, p. 361 (1882).  
n. cii, p. 571 (1857).  
n. *Phys.* xlix, p. 269 (1857).  
n. cii, p. 598 (1857).

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gust 1869, p. 95.

Measuring the Surface-Tension of Liquids.

3

contact-angle in some cases in which the wall is wet by the liquid. In support of this assertion he gives the result of a large number of measurements of bubbles and drops, from which the surface-tension is found to be considerably greater than the values found from the measurement of elevations in capillary tubes. For water at 25° C. the mean of a small number of measurements, which differ from each other by ten per cent. in some cases, gives \*  $T = 81$  dynes (84.5 at zero). Worthington† points out that Quincke's formula is only roughly approximate under the conditions of his measurements, and recalculates some of his results. The number 81 is thus reduced to 72.1 (75.6 at zero). Magie‡ prefers the value 77.6 (81.1 at zero), calculating from the same data. From his own measurements of drops and air-bubbles Magie§ found for water  $T = 71.9$  dynes at 22° 5 C. (75.1 at zero). Timberg|| from similar measurements found  $T = 80.5 - .182t$  for water. Bravais¶ and others have used the same method for other liquids. The discussion regarding these results has put a premium on methods which are independent of a contact-angle and whose mathematical relations are undisputed.

Buy's-Ballot\*\*, who made a large number of determinations of the surface-tension of water between 10° and 97° 8 C. by adhesion-disks, calls attention to the rapid decrease in the adhesion of the disk as the boiling-point is approached. This is no doubt due to disengagement of vapour near the surface of the disk, and may perhaps be an indication that the water was not completely deprived of air. Buy's-Ballot gives  $T = 75.1 - .236t$  dynes. Merian†† objects both to the calculation and to the formula used, and calculates from the same data  $T = 78.5 - .253t$ . Hagen‡‡ finds by this method a result much too low for the tension of pure water. Weinberg§§ finds  $T = 80.1 - .177t$  dynes. Miss Poekels||| obtained some interesting qualitative results with very simple apparatus.

The surface-tension has been calculated from the weight of drops falling from a small disk or tube of known perimeter by Hagen¶¶, Timberg\*\*\*, and others. Quincke††† found in a

\* Quincke, *Pogg. Ann.* cxxxix, p. 1 (1870); *Phil. Mag.* April 1871, p. 253.

† *Phil. Mag.* July 1886, p. 51.

‡ *Wied. Ann.* xxv, p. 437 (1885). § *Phil. Mag.* Aug. 1888, p. 171.

|| *Wied. Ann.* xxx, p. 545 (1887). ¶ *Ann. Chim. Phys.* v, p. 492.

\*\* *Pogg. Ann.* lxxi, p. 191 (1847). †† *Ibid.* lxxiii, p. 485 (1848).

‡‡ *Ibid.* lxxvii, p. 464 (1849).

§§ *Beibl.* xvi, p. 496 (1892); *Journ. de Physique*, Sept. 1892, p. 378.

||| 'Nature', xliii, p. 437 (March 1891).

¶¶ *Pogg. Ann.* lxxvii, pp. 449, 453 (1849).

\*\*\* *Wied. Ann.* xxx, p. 545 (1887).

††† *Pogg. Ann.* cxxxv, p. 621 (1868).

similar way the tension of metallic wires at or near their melting-points.

From measurements of pendent drops of water Worthington\* found  $T = 75$  dynes at  $16^{\circ}$  C. (77 at zero).

Henry† and Voille‡ measured the contractile force of soap-bubbles formed on U-tubes.

Dupré§ suggested that the existence of a distinct tension in a soap-film might be shown by its effect upon a straight wire laid across the legs of another U-shaped wire when a film is formed between.

Van der Mensbrugghe|| had already measured the tension of such a film in a wire frame by finding the weight supported by the free end of a string which was fastened to the frame and looped within it, so that the film was bounded by the greater part of the wire frame together with the outer edge of the circular loop.

Van der Mensbrugghe¶ also added weights to the lower of two equal horizontal circular wire rings until the barrel-shaped bubble formed between them became cylindrical. Sondhauss\*\*, who employed the same method, dispensed with the lower ring and suspended the upper from the arm of a balance above the liquid. In this way he obtained as an approximation  $T = 76 - 186t$  dynes for water between  $1^{\circ}6$  and  $16^{\circ}6$  C. Timberg†† found  $T = 80.8 - 221t$  dynes, using for calculation the maximum increase of weight as the ring is raised from the water-surface. Cantor‡‡ calculated the ratio of the maximum weight to the surface-tension, and found for water  $T = 72.3$  dynes at a temperature not stated.

Terquem§§ connected the ends of a horizontal wire by two equal strings to the ends of another wire of the same length above it. He then hung a small weight to the lower wire and measured the curvature of the strings when a film was formed between them.

Magie||| measured the curvature of the lower part of the meniscus in a capillary tube, and concluded that if any contact-angle exists at all when the liquid wets the tube it is very small. He found for water at  $19^{\circ}25$  C.,  $T = 70.9$  dynes ( $73.6$  at

\* Proc. Roy. Soc. xxxii. p. 362 (1881); Phil. Mag. Jan. 1885, p. 46.

† Phil. Mag. June 1845, p. 363.

‡ Journ. de Physique, iv. p. 313.

§ Théorie mécanique de la Chaleur, 1860.

|| Phil. Mag. April 1867, p. 270.

¶ Ibid.

\*\* Pogg. Ann. Erg. viii. (1878) p. 266.

†† Wied. Ann. xxx. p. 545 (1887).

‡‡ Ibid. xlvii. p. 399 (1892).

§§ Journ. de Physique, vii. p. 406 (1878).

||| Wied. Ann. xxv. p. 432 (1885).

zero) as compared with 71.0 by the common method at the same temperature.

Wilhelmy\* weighed a rectangular plate of known dimensions and specific gravity when dipped a determinate distance into the liquid. He made a large number of determinations which agreed closely for any one plate, but varied greatly for plates of different materials in the same liquid. Using a glass plate in water at 0° C he found  $T = 77.9$  dynes, assuming that the angle of contact is zero.

Waterston† and Worthington‡ modified Wilhelmy's method, touching only the lower edge of the plate to the liquid surface.

Sentis§ measured with a spherometer the height of a weighed and measured rectangular iron plate floating on mercury, eliminated the irregularity due to the corners by means of a second plate of the same thickness and density, and deduced the value of the surface-tension of the mercury.

Lenard|| arranged a regular succession of falling drops so as to be seen by intermittent light; measured the extent and time of their oscillations; and from these data calculated the surface-tension. For water he found  $T = 70.3$  dynes at 16° C. (72.6 at zero), the mean of a considerable number of determinations. With reasonable care in this method a clean surface is ensured, and no question of contact-angle interferes with confidence in the results.

Rayleigh¶ measured the wave-length of the transverse vibrations of water-jets issuing under constant pressure from elliptical orifices. The results, which are not closely concordant, are in harmony with the supposition that the surface-tension is about 76 dynes.

Rayleigh\*\* also measured the wave-length of ripples and calculated the surface-tension by Thomson's formula. Particular attention was given to the purity of the water-surface, and the results appear to be free from constant errors. Individual determinations differ by 2 dynes in a few cases. The mean of all, for both distilled water and tap water, is  $T = 73.9$  dynes at 18° C., corresponding to 75.4 at zero, which happens to be exactly the mean of all the results quoted for capillary tubes.

The correctness of the assumption formerly made, that when a liquid wets a solid the angle between the two surfaces may be considered zero, is now pretty well established.

\* Pogg. Ann. cxix. p. 186 (1863).

† Phil. Mag. Jan. 1853, p. 4.

‡ Ibid. Jan. 1885, p. 43.

§ Journ. de Phys. ix. p. 384 (1890); or Phil. Mag. Dec. 1891, p. 564.

|| Wied. Ann. xxx. p. 200 (1887).

¶ Proc. Roy. Soc. xxix. p. 71 (1879).

\*\* Phil. Mag. Oct. 1890, p. 386.



None of the methods in use seem to exceed in general accuracy or convenience the ordinary plan with capillary tubes, the limitations of which have been already referred to. The direct dependence of surface-tension upon molecular cohesion, and its consequent importance as a reliable indication of changes of condition in liquids, makes it very desirable that some more accurate plan of measurement should be devised.

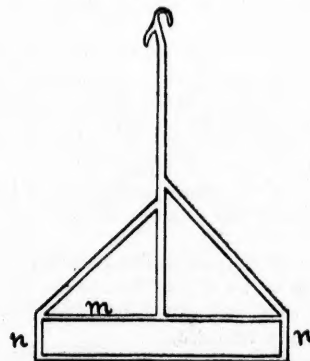
## II. NEW METHODS.

### A.

Two years ago, at the suggestion of Professor Michelson and under his direction, I undertook the investigation of a direct method which, from some preliminary experiments, he expected to give results ten times as accurate as those found by any method now in general use.

This method consists in finding the weight of a thin horizontal bar, suspended a few millimetres above the liquid surface, whose extremities are bent at a right angle so as to dip into the liquid. The weight is taken first when a film of the liquid is extended between the bar and the level surface, and, secondly, in exactly the same position after the film is broken. The difference between the two weights divided by twice the width of the film gives the surface-tension in grams per centimetre, which is reduced to dynes per centimetre when

Fig. 1.



multiplied by the constant  $g$ , whose value at Clark University is 980.3.

For nearly all ordinary liquids a glass rod is suitable, but

a rod of almost any material sufficiently rigid which is wet by the liquid will serve as well. For mercury a steel needle plated with copper and well amalgamated has been suggested. In my investigations the rod was of glass, and formed part of a glass frame (fig. 1) whose form was varied to suit the circumstances. The essentials of a good frame are the following:—

- (a) It must not yield sensibly under the tension of the film.
- (b) The bar  $m$  must be thin, and all parts of  $m$  and  $n$  must lie evenly in the vertical plane.
- (c) The frame must be balanced so that  $m$  hangs horizontally both with and without the film.
- (d) The two short sides,  $nn$ , must be of uniform and nearly equal diameter, must be as nearly as possible parallel, perfectly straight, and make sharp right angles with  $m$ .

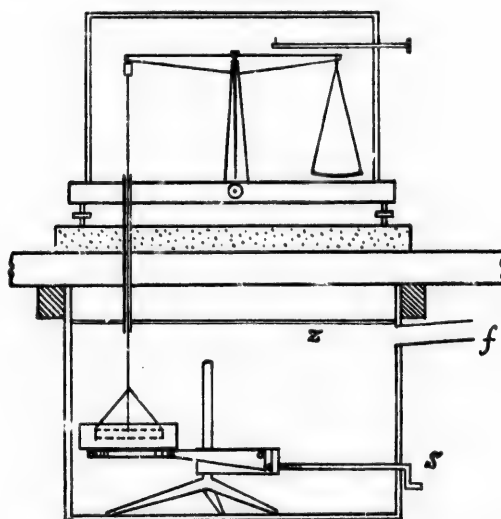
With a little practice and more patience good frames were readily made in the following way. Taking ten centimetres of a small hard-glass tube, I bent it at a right angle near one end, then fused that end until only a minute hole with a very thick margin was left. This was connected by a thin rubber tube to a gas-pipe, and the small jet lighted. It burned with a clear blue flame 10 to 15 millim. long, and quite hot enough to melt glass rods a millimetre in diameter. If the orifice is too large the flame has a white tip and is not so hot. An improved jeweller's blowpipe connected by slender rubber tubes to the gas-supply and to the mouthpiece will do nearly as well. This blowpipe is held in the hand. Glass threads of suitable size are laid upon an asbestos mat, which has a number of pencil lines drawn upon it exactly at right angles, and are there fused together in the required form. For general use a frame like the one shown in the figure may be made of rods  $\frac{1}{4}$  to 1 millim. thick (the handle thicker); having the bar  $m$  10 centim.,  $n$  2 centim., and the handle 15 to 20 centim. long. In some cases the lower horizontal bar may be omitted with advantage.

The frames were measured along lines parallel to  $m$ , between the inner edges of  $nn$ , at measured distances from  $m$ . If  $nn$  were not nearly parallel they were reset with the hand blowpipe. The measurements were made by comparison with a standard metre bar on the bed of a dividing-engine, where it was easy to get a degree of accuracy in excess of what was required for this investigation.

Figure 2 is a diagram of the general arrangement for weighing the tension. The balance stood upon a marble slab on a high shelf projecting from a brick partition-wall of the

laboratory. Under the shelf was a wooden closet having a door in front, a zinc top, *z*, and a pipe, *f*, leading to a ventilating-flue. The liquid to be examined was placed in a deep

Fig. 2.



glass evaporating-dish, which sometimes was fitted with a ground-glass cover, and rested upon the specially constructed arm of a heavy retort-stand, so arranged that it could be raised or lowered several centimetres by turning the screw-handle, *s*, outside the closet. Arrangements were also made for stirring the liquid by twirling in the fingers the end of a long-handled glass stirrer (fig. 3), and also for changing the glass frames, without opening the closet-door.

The liquid was placed so that its surface was 10 or 15 millim. below the bar *m* (fig. 1) of the frame. The latter was lowered into the liquid by tipping the balance-beam.

For work in which an error due to a change of half a degree in temperature may be neglected, such an arrangement is very satisfactory. But if it is desired to find the surface-tension at high or low temperatures, and especially

Fig. 3.



if the greatest attainable accuracy is desired, I should advise a different arrangement. A deep, thin-walled glass dish with a close-fitting cover in which are three holes—one in the centre for the arm of the frame, one for the thermometer, and one for the stirrer—should fit loosely into a double-walled box, also partly covered over the top, within which are air- or water-pipes, resistance-coils, or other arrangement for controlling the temperature. The large wooden closet of figure 2 may then be replaced by a simple subshelf for the box. For volatile liquids it is necessary to keep a slow current of air passing down the tube from the balance, to prevent condensation of the liquid on the rod that carries the frame.

A small correction is required for the capillarity of the sides  $nn$  of each frame. When the film is broken after the first weighing, a capillary elevation remains completely surrounding each side,  $n$  (fig. 1). But our calculation of the tension is based on the assumption that during the second weighing no tension is exerted at all between the sides  $nn$ . In effect, the difference between the two weighings gives the tension of a film a little narrower than the frame. The amount of this correction was found by taking the tension of the same liquid with two or more frames of the same thickness but of different widths. An example will explain the method.

The surface-tension of distilled water at  $19^{\circ}5$  C. was measured with three frames, whose widths  $a$ ,  $b$ ,  $c$ , and whose tension-weights  $m$ ,  $n$ ,  $r$ , were respectively

$a=5.2321$ centim.	$m=.7742$ gram.
$b=2.0325$ „	$n=.3001$ „
$c=0.2037$ „	$r=.0291$ „

Disregarding the capillary correction, the resulting values for the surface-tension in grams per centim. are :—

$$\frac{m}{2a} = .073985,$$

$$\frac{n}{2b} = .073825,$$

$$\frac{r}{2c} = .0714.$$

The true value of the tension, however, is

$$T = \frac{m}{2(a-x)} = \frac{n}{2(b-x)} = \frac{r}{2(c-x)}.$$

Fig. 3.



Eliminating  $x$  by the principle of proportion,

$$T = \frac{m-n}{2(a-b)} = \frac{m-r}{2(a-c)} = \frac{n-r}{2(b-c)};$$

also

$$x = a - \frac{m}{2T} = b - \frac{n}{2T} = c - \frac{r}{2T};$$

from which the following values are obtained :—

T (gram).	$x$ (centim.).
·074089	·0074
·074088	·0073
·074092	·0073
Mean ... ·074090	·0073

The value of  $x$ , for rigid frames, depends almost wholly upon the thickness of the vertical sides  $nn$ . If the frame be so slender as to allow these sides to approach each other sensibly under the tension of the film, the value of  $x$  will be increased. The following results were obtained in the course of my work :—

Widths of frames, in centim.	Thickness of sides (centim.).	Liquid.	T (dynes).	$x$ (centim.).	Notes.
5·23 2·03 0·20	·025 to ·029	Water.	72·6	·0073	Frames nearly rigid.
11·76 0·92	·038 to ·040	"	72·8	·0073	Rigid.
11·22 1·06	·076 to ·080	"	73·4	·0191	"
"	"	50 per cent. alcohol.	30·3	·0186	"
11·88 0·96	·028 to ·033	Water.	72·9	·0136	Slender.
"	"	"	"	·0139	"

The capillary correction for a rigid frame 10 centim. wide, whose vertical sides are half a millimetre thick, does not exceed 1 part in 1000.



The weight required to balance a film of soap solution increased slightly for some time after its formation. The apparent tension of films of glycerine and of strong sulphuric acid decreased, at first rapidly, then more and more slowly for several minutes, finally becoming sensibly constant. The whole amount of increase or decrease after the first few seconds was generally about .02 per cent. of the tension.

The apparent tension of a film of water was in all cases sensibly constant as long as the film lasted. This seems remarkable when it is remembered that the water-film must have been growing thinner by evaporation, and also that the water under the bar *m* and along the sides *nn* was gradually flowing down into the liquid. The first process tended to decrease the weight very little and to increase the surface-tension by lowering the temperature; the second to decrease the weight. A change of one part in ten thousand could be readily detected.

The second weight—the weight of the frame *plus* adherent water after the film is broken—is variable. If the film is broken two or three seconds after its formation, the weight of the frame may be two or three milligrams greater than it is when the film lasts ten seconds. But the differences when the film has lasted more than five or six seconds are very small, amounting to only one or two tenths of a milligram for a frame 10 centim. wide.

This variability in the second weighing marks the limit of accuracy of the method as about one part in 5000, or .02 per cent., though a change in the tension amounting to less than .01 per cent. may be readily measured.

It will be shown later that the bar *m* must be raised from five to ten millimetres above the liquid surface before a true film is formed, and that the tension is not correctly found at a less height. It follows that the tension of alcohol, ether, chloroform, and similar liquids, in which the film breaks almost instantly at such a height, cannot be found by this method.

#### B.

In order to find the surface-tension of such liquids I adopted a modification of Wilhelmy's method. When the edge of a thin vertical plate is touched to a liquid surface, the liquid usually rises along the line of contact, and the weight of the plate is increased by

$$w = 2(a+b)T \cos \theta,$$

where *a* is the length and *b* the thickness of the plate in centimetres, *T* the surface-tension in grams per centimetre,

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Notes.
Frames nearly rigid.
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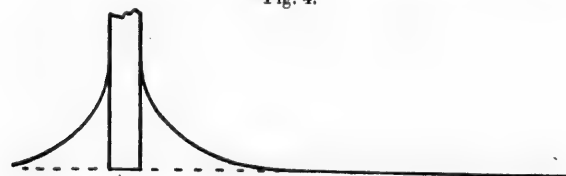
tim. wide,  
does not

and  $\theta$  the contact-angle. When the plate is wet by the liquid,

$$\theta = 0 \text{ and } w = 2(a+b)T.$$

When the lower edge of the plate is kept at the general level of the surface, as in fig. 4, the thickness of the plate

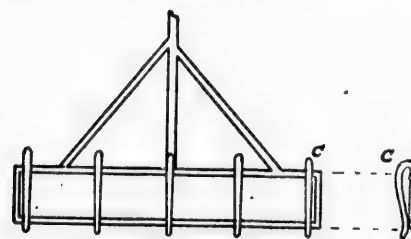
Fig. 4.



is of no consequence; but if it be placed  $h$  centimetre too high or too low there will be an error introduced equal to the weight of the liquid supported under the plate or displaced by it. That is to say, if  $\rho$  be the density of the liquid and  $h$  positive when the plate is too high, an error of  $abh\rho$  gram is introduced. This error becomes very small without material alteration in  $w$  when the plate is made very thin. In practice I found that for a plate 10 centim. long  $h$  rarely exceeded  $\pm 0.1$  centim., and that the amount of this error of setting for a plate  $0.005$  millim. thick was not more than  $\frac{1}{10}$  milligram; or, for alcohol, about  $0.1$  per cent. of the surface-tension.

Thin plates were placed in a holder (fig. 5) made of glass

Fig. 5.



rods 1 millim. thick. Before inserting a plate the holder was balanced so that the stem hung vertically. The spring clips  $c$  (also of glass) were then wedged with little bits of wood, the plate inserted under them, two of the clips released, and the plate adjusted by trial over a liquid until the whole

edge seemed to enter the liquid at once when lowered, and when raised slowly parted from the liquid first at the two ends and lastly in the middle of the lower edge. After adjustment the holder and plate were washed, dried over a Bunsen flame, attached to the balance in the same way as the frame (fig. 2), left hanging over the liquid to be examined until the temperatures were nearly the same, then weighed. The index of the balance was next set exactly at zero, taking care that the beam was not lifted, and the liquid slowly raised by turning the screw-handle *s* until it touched the plate. The weight was again adjusted to bring the index exactly to zero. For a second determination the plate was lifted out of the liquid by tipping the balance-beam, the liquid lowered a little, and after all visible disturbance of the surface had ceased the operation of setting was repeated. The surface-area of the liquid must be so great that the measurement is not sensibly increased by the lowering of level due to the capillary elevation; or else this must be taken account of in the calculation.

It was necessary to ascertain, in the first place, whether the contact-angle can be considered zero to the limit of accuracy attainable by this method, and if so under what conditions. I proceeded to try plates of various materials in some liquids whose tension could be found by Michelson's method.

(1) *Glass Plate in glycerine.*

A microscope cover-glass, 5.044 centim. long and .026 centim. thick, was cleaned, dried, and touched to the glycerine surface without being allowed to sink even momentarily deeper. The first three weighings were made rapidly; the last three after an hour's contact.

	<i>w</i> (gram).	$T \cos \theta$ (dynes).	Temp. C.
1.	.6405	61.92	16.6
2.	.6391	61.79	"
3.	.6420	62.06	"
4.	.6550	63.32	16.9
5.	.6536	63.07	"
6.	.6534	63.12	"

The tension, as found by Michelson's method immediately afterwards, was

63.14 dynes at 17° C.

The error of setting calculated for this plate is  $\pm 0.13$  dyne. The angle of contact may therefore be considered zero for glycerine and glass if time is allowed for attaining equilibrium.

(2) *Platinum in glycerine.*

In the same liquid a platinum plate, 6.375 centim. long, .0045 centim. thick, was touched to the surface and let stand a few minutes.

<i>w.</i>	<i>T cos <math>\theta</math>.</i>	Temp. C.
.8234	63.26	16.0

The error of setting is  $\pm 0.02$  dyne.

(3) *Glass Plate in tap-water.*

The same plate as in (1).

<i>w.</i>	<i>T cos <math>\theta</math>.</i>	Temp. C.
.7585	73.33	14.52
.7581	73.29	14.55
.7583	73.31	14.58

*T*, by frame, = 73.32 at 14.41.

(4) *Platinum in tap-water.*

The plate used in (2) in the liquid of (3).

<i>w.</i>	<i>T cos <math>\theta</math>.</i>	Temp. C.
.8618	.....	.....
.9541	73.30	14.8
.9535	73.28	"
.9538	73.28	"

The first weight was taken with the same precautions as before to prevent dipping below the water-level. In the other three cases the plate was dipped 1 millim. into the water, to wet it. The correction for  $-0.4$  is  $+0.06$  dyne, which makes the mean of the last three results 73.34 dynes at 14.4.

(5) *Platinum in distilled water.*

Plate the same as in (2), dipped 1 millim.

<i>w.</i>	<i>T cos θ.</i>	Temp. C.
·9536	73·26	15·28
·9544	73·32	15·10

The mean of these corresponds to 73·31 dynes at 15°·04, at which the tension was found by a frame to be 73·36 dynes.

Another trial with water freshly boiled gave with the plate

$$T \cos \theta = 72·10,$$

and with a frame

$$T = 72·76,$$

both at 19°·9 C.

In all these cases the platinum plate was washed with a caustic soda solution, well rinsed either in distilled water or at the tap, and made red-hot in a Bunsen flame before touching the liquid. I found that if the plate touched the liquid surface before it had time to cool after leaving the flame, the contact-angle would remain (sensibly) zero for a few minutes, without dipping the plate at all. It seems probable that condensation of air upon the plate may be one cause of the failure to get a zero angle. When the plate was washed without alkali, with or without acids, I failed to make the contact-angle even approximate to zero.

(6) *Platinum in a dilute solution of caustic soda.*

Plate the same as in (2).

<i>w.</i>	<i>T cos θ.</i>	Temp. C.
·9023	69·32	16·24
·9019	69·29	16·24
·9019	69·29	16·22
·9019	69·29	16·20

By a frame,  $T = 69·36$  dynes at 16°·17.

(7) *Silver plate in distilled water.*

This plate was 7·625 centim. long, ·0025 centim. thick. It was washed in caustic soda solution, then in water, and dipped 1 millim. into the liquid before each weighing.



	<i>w.</i>	$T \cos \theta$	Temp. C.
1.	1.0000	64.27	17.70
2.	1.0030	64.46	"
3.	1.0035	64.49	"
4.	1.0050	70.37	18.00
5.	1.0855	69.76	17.70
6.	1.0850	69.73	"

By a frame,  $T = 72.84$  dynes at  $18^{\circ}.37$ .

Before the fourth weighing the plate was warmed over a Bunsen flame, touched immediately to the water surface, and allowed to remain in contact ten minutes. 5 and 6 were taken after two hours of contact.

(8) These results, along with some others of the same kind, show that the contact-angle can be considered zero for

Glass and water, sulphuric acid, glycerine,  
Mica and water,  
Zinc and water,

when the surfaces are clean, and, in the case of zinc, freshly shaved; and that the angle for

Platinum and water,  
Silver and water,

can be made zero, or nearly zero, with certain precautions.

In every case it is easy to see by a glance along the line of contact in a good light whether the angle of contact is zero or not.

(9) Though there could be no reasonable doubt that the angle of contact for alcohol and similar liquids would be zero in nearly all cases, as some observers have supposed otherwise I thought it worth while to measure the surface-tension of alcohol by several different plates. If there is a finite contact-angle for each plate, the values found for  $T \cos \theta$  will be different. If these values are all alike, it is reasonably certain that the contact-angle is zero. The following table gives the results. In no case was any difference found in the weight after dipping the plate one or two millimetres into the alcohol, provided the plate was then allowed to stand two or three minutes in the normal position. During the operations the surface-tension probably increased a little by absorption of water-vapour from the air.

## Common Alcohol.

Plate.	Length (centim.)	Thick- ness (centim.)	$T \cos \theta$ (dynes).	Temp. C.	$T \cos \theta$ at 16° C.	Variation from mean of (1) and (2).	Error of setting, calcu- lated.
Platinum (1)	6.375	.0045	23.38 23.38	15.80 "	23.36 23.36	-.02 -.02	.02 dyne.
Zinc .....	12.3085	.0105	23.52 23.53	15.90 15.92	23.51 23.52	+.13 +.14	.05 "
Silver .....	7.625	.0025	23.56 23.57	16.00 "	23.56 23.57	+.18 +.19	.01 "
Tin .....	11.480	.004	23.34 23.34	16.20 16.24	23.36 23.36	-.02 -.02	.02 "
Glass .....	5.044	.026	23.40 23.41	16.30 "	23.43 23.44	+.05 +.06	.10 "
Platinum (2)	13.481	.002	23.37 23.37	16.43 "	23.40 23.40	+.02 +.02	.01 "

The zinc plate was slightly wedge-shaped and not very regular on the edge. There was no such irregularity in the silver plate; but on watching closely I could see that the alcohol crept rapidly up the plate, wetting it to a height of several millimetres above the normal line of contact. Several other trials with a silver plate showed the same peculiarity. There may have been something similar happening on the zinc plate, but if so I failed to detect it. Mica plates give the same result as plates of platinum and glass.

A platinum plate, if it can be obtained of the right thickness, is most satisfactory for liquids like alcohol. But mica makes a very good substitute. Mica can be split into sheets 10 or 15 centim. square and less than one hundredth of a millimetre thick by a thin paper-knife under water. The thin sheets may be floated upon sheets of paper, taken out and left to dry. They are easily cut with the point of a sharp knife when lying under a sharp-edged rule upon a glass plate; but they require rather delicate handling at every stage.

One of the difficulties of this method is caused by the tendency of minute specks, if there be any on the liquid surface, to gradually collect upon the plate and affect the measurement more than they affect the tension of the whole surface. A platinum plate should therefore be occasionally heated in the Bunsen flame, and for this reason it is convenient to have the plate in a metal holder. On a mica plate the effects of

dust &c. are more easily seen, but it requires careful washing with a soft brush.

Under favourable conditions—a fresh clean surface, constant temperature, no dust, no disturbing vapours—a high degree of accuracy is attainable by this method. The following are selected from my results when these conditions were most nearly fulfilled.

1. Platinum plate, 13.495 centim. long, .0045 centim. thick, in 99.8 per cent. alcohol. Error of setting, calculated, .02 dyne.

w.	T (dynes).	Temp.
.6210	22.548	18.22
.62095	22.543	18.25
.6209	22.537	18.29
.6209	22.537	18.31

The temperature-correction for 0°.1 is —.008 dyne.

2. Mica plate, 11.3180 centim. long, .0007 centim. thick, in common alcohol at 17°.20 C. Calculated error of setting, .003 dyne.

w.	T (dynes).
.55304	23.949
.55307	23.950
.55306	23.950

3. Mica plate, 11.42285 centim. long, .0004 centim. thick, in common alcohol. Calculated error of setting, .002 dyne.

w.	T (dynes).	Temp.
.56360	24.183	16.20
.56363	24.184	16.24
.56363	24.184	16.26

C.

It has been already stated that, in order to form a true film between the liquid and the bar *m* of the frame (fig. 1), this bar must be from five to ten millimetres above the level surface. Even when the bar is excessively thin a distinct

maximum of weight is noticeable as the frame is raised, just before the true double-film is formed. This maximum can be found very exactly, and is made the basis of a third method of measuring surface-tension.

An equation to the capillary curve is found in the expression of the fact, that the vertical component of the surface-tension at any point is equal to the weight of liquid raised above the level surface, by the curved surface, from the level up to a perpendicular through that point. That is to say, taking a section of the capillary elevation of unit thickness (fig. 6),

$$T \sin \alpha = g\rho \int_{-x}^x y dx, \quad \dots \dots (1)$$

where

$\alpha$  = the angle made by the tangent with axis of  $x$  (the level surface);

$T$  = the surface-tension, in dynes per centim.;

$\rho$  = the liquid density;

$g$  = the constant of gravitation.

If  $c^2 = 4T/g\rho$ , then

$$\frac{dx}{d\alpha} = \frac{c^2}{4y} \cos \alpha.$$

And since  $\tan \alpha = dy/dx$ ,

$$\therefore \frac{dy}{d\alpha} = \frac{c^2}{4y} \sin \alpha.$$

Integrating,

$$\cos \alpha = \frac{c^2 - 2y^2}{c^2}; \quad \dots \dots (2)$$

$$\therefore \frac{dy}{dx} = \tan \alpha = \frac{\pm \sqrt{1 - \cos^2 \alpha}}{\cos \alpha} = \frac{\pm 2y \sqrt{c^2 - y^2}}{c^2 - 2y^2}.$$

Integrating again,

$$\pm x = \frac{c}{2} \log \frac{c + \sqrt{c^2 - y^2}}{y} - \sqrt{c^2 - y^2} + C.$$

Taking the origin so that the axis of  $y$  is tangent to the curve, when  $x=0$ ,  $y^2=c^2/2$ , from (2), and therefore

$$\pm x = \frac{c}{2} \log \frac{c + \sqrt{c^2 - y^2}}{y} - \sqrt{c^2 - y^2} + \frac{c}{2} \{ \sqrt{2} - \log (\sqrt{2} + 1) \}. \quad (3)$$

Suppose a horizontal circular cylinder of density  $\rho$ , whose diameter may be neglected in comparison with its length, to be suspended from one arm of a balance and to be in equilibrium just below the surface of a liquid, of density  $\rho$ , which wets it. When the cylinder is raised through a distance  $h$ ,

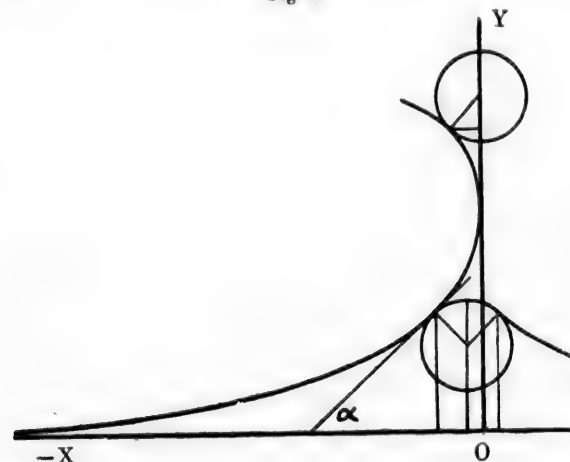
the increase of weight is  $\rho$  times the volume of cylinder and of liquid raised above the level surface. If  $r$  be the radius of the cylinder and  $w$  the increase of its weight, in grams, then (fig. 6) for unit length of the cylinder,

$$wg = 2T \sin \alpha + 2r\rho y g \sin \alpha + r^2 \rho g \alpha - r^2 \rho g \sin \alpha \cos \alpha,$$

$$\text{or } w = \rho \left\{ \frac{c^2}{2} \sin \alpha + 2ry \sin \alpha + r^2 \alpha - r^2 \sin \alpha \cos \alpha \right\}, \dots (4)$$

where  $xy$  is a point of contact of the cylinder and the surface film.

Fig. 6.



We have also (fig. 6)

$$h = y + r - r \cos \alpha, \dots (5)$$

$$\therefore h = y + \frac{2r}{c^2} y^2 \dots \text{from (2)},$$

$$\therefore y = \frac{c}{4r} (\sqrt{c^2 + 8rh} - c) \dots (6)$$

Equations (4), (5), and (6) are sufficient to determine  $w$  when  $h$ ,  $r$ ,  $\rho$ , and  $T$  are given.

The condition that  $w$  shall be a maximum is that  $dw/dh = 0$ .

Now

$$\begin{aligned} \frac{dw}{dh} &= \frac{dw}{d\alpha} \cdot \frac{d\alpha}{dh} \\ &= \frac{d\alpha}{dh} \rho \left\{ \frac{c^2}{2} \cos \alpha + 2ry \cos \alpha + 2r \sin \alpha \frac{c^2 \sin \alpha}{4y} + 2r^2 \sin^2 \alpha \right\}, \end{aligned}$$



and putting for  $\cos \alpha$  and  $\sin \alpha$  their values from (2), the condition that  $w$  shall be a maximum is

$$16r^2y^4 + 12c^2ry^3 + 2c^3(c^2 - 8r^2)y - 8c^4ry - c^6 = 0. \quad (7)$$

The numerical value of  $y$  may be found in any particular case by assuming that when  $w$  is a maximum  $\alpha = \frac{\pi}{2}$ , and finding for  $c^2$  from (4) an approximate value to use in (7).

$h$  is a maximum when  $dh/dw = 0$ , in which case  $\alpha = \pi$  and  $w = \pi r^2 \rho$ . But before this condition is attained the liquid surfaces meet below the cylinder and form (in some cases) a film. This occurs when (fig. 6)

$$\mp x = \pm r \sin \alpha,$$

$$= \pm \frac{2yr}{c^2} \sqrt{c^2 - y^2}, \text{ from (2),}$$

$$= \frac{c}{2} \log \frac{c \pm \sqrt{c^2 - y^2}}{y} - \sqrt{c^2 - y^2} + .51572 c, \text{ from (3),}$$

or

$$\log \frac{c - \sqrt{c^2 - y^2}}{y} = \left( \frac{4ry}{c^2} + \frac{2}{c} \right) \sqrt{c^2 - y^2} - 1.03144, \quad (8)$$

from which  $y$  may be found approximately in terms of  $c$  and  $r$  by trial. The required value of  $y$  is greater than  $c/\sqrt{2}$  and less than  $c$ , hence the selection of signs in (8).

As soon as a true film is formed having plane surfaces, the quantity  $2ry \sin \alpha$  in (4) is reduced to  $2r \sin \alpha (y - c/\sqrt{2})$ , because the column of liquid below the film no longer acts directly to produce a (negative) pressure upon the bottom of the cylinder; and  $w$  is reduced to  $2T$  plus the weight of the cylinder and of the small quantity of liquid suspended under the cylinder and above the film.

Up to this point the ends of the cylinder, which in practice must be turned down, have been disregarded. Their effect may be eliminated by the use of a long and a short cylinder having the same thickness and their ends alike; but if the bend is like an elbow, or is made by a rectangular prism abutting squarely on the end of the cylinder, the effect of the ends may be calculated.

Taking the former case, let  $l$  (fig. 7) be the whole length of the cylinder along the dotted line,  $r$  its radius,  $h$  as before the height of the top of the horizontal cylinder above the general level of the liquid, and  $k$  the length of each vertical end-piece, measured from the top. Equation (4) may be applied over the length  $l - 2r - \pi r/2$ . And if we subtract

the weight of liquid displaced by the cylinder, the increase in

Fig. 7.



weight over the weight of the frame in air is, for this central part,

$$(l-2r-\pi r/2)\rho \left\{ \left( \frac{c^2}{2} + 2ry \right) \sin \alpha + r^2(\alpha - \pi) - r^2 \sin \alpha \cos \alpha \right\}.$$

To this is to be added the surface-tension around the vertical ends, and also the weight of liquid supported under them above the level of the surface; making as a very close approximation the whole increase of weight to be  $W$ , where

$$W/\rho = (l-2r-\pi r/2) \left\{ \left( \frac{c^2}{2} + 2ry \right) \sin \alpha + r^2(\alpha - \pi) - r^2 \sin \alpha \cos \alpha \right\} + \pi r c^2 + 2\pi r^2(h-k). \quad (9)$$

In the following table are given the observed weights with a somewhat irregular glass frame, along with the calculated values of the four terms on the right of equation (4) for the same height  $h$ , in grams per centim. The liquid was water, whose density is assumed as unity.

$r = .0375$  (mean);  $l = 9.76$ ;  $T = .07395$  gram per centim.

$h$ (mm.).	$w$ , obs.	$\alpha$ .	$2T \sin \alpha$ .	$2ry \sin \alpha$ .	$r^2 \alpha$ .	$-r^2 \sin \alpha \cos \alpha$ .	$w$ , calc.
$\frac{1}{2}$	.0100	18° 47'	.0352	.0012	.0003	-.0003	.0364
2	.1042	41° 4'	.0672	.0149	.0010	-.0007	.1124
$3\frac{1}{2}$	.1547	69° 16'	.1383	.0217	.0017	-.0005	.1612
4	.1724	84° 29'	.1472	.0273	.0021	-.0001	.1765
$4\frac{1}{2}$	.1755	92° 49'	.1477	.0298	.0023	+.0001	.1799
$4\frac{3}{4}$	.1763	97° 9'	.1468	.0304	.0024	+.0002	.1798
†	—*	90° 42'	.1458	.0307	.0025	+.0003	.1793
$4\frac{3}{4}$	.1755						
$4\frac{1}{2}$	.1739						
5	.1722						
$5\frac{1}{2}$	.1579						
$5\frac{3}{4}$	.1547						
$5\frac{1}{2}$	.1520			$2r \sin \alpha (y - c/\sqrt{2})$			
6	.1520	...	.1458	.0023 †	.0025	+.0003	.1509

\* During the next five weighings the balance was in unstable equilibrium.

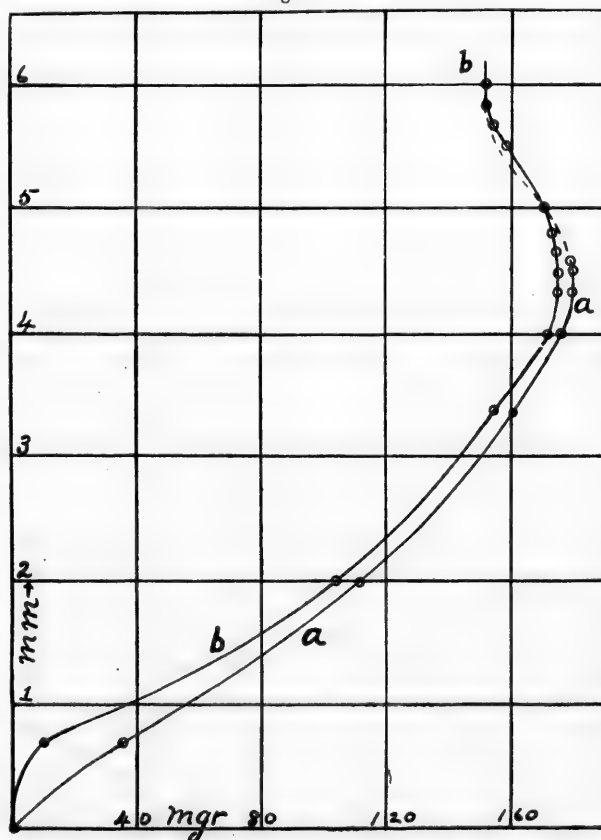
† The numbers in this row are calculated from the value of  $y$  found from equation (8), and are for the point at which the two liquid surfaces meet below the bar.

‡ See the paragraph following equation (8).

To the last calculated value of  $w$  is to be added '0005 for the displacement of the two end-pieces of the frame, leaving + '0006 per centim. to account for the surface-tension about the (irregular) ends.

In fig. 8 the curves  $a$  and  $b$  represent the calculated and observed values of  $w$  given in the table. The calculated

Fig. 8.



curve,  $a$ , is left incomplete because some of the factors needed for the calculation of the rest of it are uncertain. It probably should go somewhere near the dotted line.

$r^2 \sin \alpha \cos \alpha$	$w$ , calc.
-0003	0364
-0007	1124
-0005	1612
-0001	1765
+0001	1799
+0002	1798
+0003	1793
+0063	1509

This method is capable of showing a change of surface-tension with almost incredible delicacy when the frame is rigid. A single example is given below. The liquid was common alcohol, at 20°-20 C., and each weight was found with a fresh film. The increase of weight (*W*) due to the tension is given in grams. The corresponding values of *T* were not calculated.

	W.
1.....	.72422
2.....	.72420
3.....	.72424
4.....	.72422
Mean ...	.72422

Frames of this sort cannot be made with such exactness as to give practical results agreeing with those calculated to 1 part in 70,000, nor to 1 in 7000. But if the values of the surface-tension are found by either of the methods before described, and compared with  $W/\rho$  in each case, the values of *r* and *k* may be corrected for any particular frame, so that reliable results may be obtained with it for other liquids with much greater ease than by the former methods.

For this purpose put  $n=l-2r-\pi r/2$ , and  $\beta=\alpha/2$ . Then equation (9) becomes

$$2\pi r^2 \sin \beta (c + 2r \sin \beta) + n \sin \beta \cos \beta \{c^2 - 2r^2 + 4cr \sin \beta + 4r^2 \sin^2 \beta\} + r^2 n (\alpha - \pi) + \pi r c^2 - 2\pi r^2 k - W/\rho = 0. \quad (10)$$

When *W* is a maximum,

$$16r^2 n \sin^4 \beta + 12rcn \sin^3 \beta + (2c^2 - 16r^2)n \sin^2 \beta - 8rnc \sin \beta - 8\pi r^3 \sin \beta \cos \beta - 2\pi r^2 c \cos \beta - c^2 n = 0. \quad (11)$$

These equations are almost unmanageable, however, and time will be saved in most cases by disregarding them and plotting a curve of experimental values to show the relation between *T* and  $W/\rho$  for a given frame.

The convenience of this method in practice will repay the trouble of finding such a relation. While Michelson's method has the merit of directness and simplicity, its use is limited to such liquids as form a fairly stable film in air. The method of thin plates is constantly open to suspicion as to the

existence of a finite contact-angle. The maximum-weight method is free from both these objections, and can be used for almost any liquid. If the specific gravity of the liquid is not accurately known, a thin frame should be used, so that an error in the specific gravity will have small influence on the final result. For accurate results great care must be taken to prevent any oscillation of the balance as the weight approaches the maximum. Zero weighings are also essential.

### III. SURFACE-TENSION OF WATER.

In spite of the labours of a large number of investigators, the surface-tension of water is still more or less uncertain. Apart from experimental errors, which are seldom less than one half of one per cent., there is very great difficulty in retaining a pure water surface throughout the measurement. Using the methods of measurement described in Part II. of this paper, it became evident at once that the problem of finding the surface-tension of water accurately, to one tenth of one per cent. or less, was practically reduced to that of securing a clean surface and a constant temperature for pure water.

The weights used were found consistent with each other, and therefore presumably correct, to one tenth of a milligram, with two or three exceptions which were taken note of. The arms of the balance were sensibly equal, and the riders accurate. One of the mercury thermometers was graduated in half degrees, Centigrade, from  $-10^{\circ}$  to  $+100^{\circ}$ ; the other in fifths of a degree, from  $-4^{\circ}$  to  $+30^{\circ}$ . The latter could be easily read to fiftieths. The zeros of both were correct.

Some water that had been distilled repeatedly by Dr. Loeb in such a manner as to remove carbon dioxide and organic matter and ammonia, was kindly furnished by him for measurement of the surface-tension. I preserved it in a large well-washed glass bottle whose stopper and neck were covered by an inverted beaker to keep off dust.

The deep evaporating-dish already mentioned, its cover, the thermometer, and the glass frames (fig. 1) were well washed in a dilute solution of caustic soda and thoroughly rinsed, first in ordinary distilled water and secondly in some of the water that was to be examined. The ground-glass cover remained on the dish except while frames were being put in or taken out; and before each measurement the temperature of the whole was kept nearly constant for half an hour or more.

The observations extended over two days, partly because of the difficulty there was in getting a film to last long enough to be weighed. On the third day the surface-tension was so



much reduced that it was evident that the surface had become contaminated. I have reason to believe that only the first two, if any, of the observations were made with a clean surface, and have therefore in the fourth column given the values calculated by the formula

$$T = 75.48 - .140t \text{ dynes}$$

obtained by taking the first two observations only.

Weight (in grams.).	Temp. C.	T found.	T calc.	Difference.
.8044	0.1	75.468	75.468	
.7859	12.5	73.733	73.730	
.7836	13.8	73.52	73.55	.03
.7795	16.2	73.13	73.21	.08
.7742	19.5	72.63	72.75	.12

The width of the frame was 5.2321 centim., and its capillarity correction .0075 centim. The same frame was used for the following observations, which were made at different times for the purpose of finding the effect of dissolved air upon the surface-tension. The first seven of the following measurements were made with fresh portions of the same water as the foregoing. In the last column they are reduced to 18° C., at which the surface-tension according to the formula given above is 72.96 dynes.

	Weight (in grams.).	Temperature.	T found.	T at 18°.
1.	.7763	18.37	72.82	72.87
2.	.7753	19.90	72.74	73.00
3.	.7748	20.60	72.69	73.06
4.	.7752	18.64	72.73	72.82
5.	.7750	19.32	72.71	72.99
6.	.7766	17.85	72.86	72.84
7.	.7772	13.35	72.92	72.87
8.	.7813	15.97	73.30	73.02
9.	.7780	17.76	72.99	72.96
10.	.7697	19.60	72.21	72.44

On several occasions water that was left in the glass dish in the closed closet over night was found next morning to have a surface-tension considerably lower than it had the night before. If left two or three days the difference was greater, even when the cover was on the dish during the whole time. But after a vigorous stirring the surface-tension was in each case a little greater than it had been at first. The substance, whatever it was, that made the change, being present in small quantity in the surface-layers of the water, reduced the tension. The same amount of the substance scattered throughout the whole volume of the water, and hence present in very minute quantity in the surface-layers, increased the surface-tension.

Some of the purified water mentioned above was boiled briskly half an hour in a covered glass beaker to expel the air. A smaller bottle was completely filled with the boiled water and left to cool. Half of it was then poured into the dish and its surface-tension measured without delay. The remaining half was shaken up with the air in the bottle, and its surface-tension measured. In the table above (2) is water freed from air, (3) the portion shaken up with air. The tension when air is present is greater by .06 dyne. (4) and (5) are similarly related, and the difference is .07 dyne. (6) was simply poured into the dish from the large bottle; and (7) was stirred vigorously in the open dish with a glass rod. (8) and (9) are two specimens of clean snow melted and not boiled. (10) is a portion of (9), well stirred, after remaining two weeks in a covered dish.

The mean of these values is one dyne less than the mean of Lord Rayleigh's results\* from measurements of the wavelength of ripples. The difference is not accounted for by the presence or absence of dissolved air, though it is probable that carbon dioxide in moderate amount would make more difference than the more perfect gases; and it seems very improbable that the difference is owing to constant errors in either of the methods. Two possible explanations remain: (1) unnoticed contaminations of the surface, and (2) real differences in the surface-tension of the different specimens of water.

In order to secure a fresh clean surface I arranged a long glass siphon to reach from a glass vessel on the shelf near the balance into the glass dish in the closet below. Its lower end was drawn out small and turned upward from the bottom of the dish so that the incoming stream continually swept the whole surface of the dish, which was tilted up at one side to

\* Rayleigh, Phil. Mag. October 1890, p. 386.

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secure a more steady overflow. The flow was at the rate of two or three litres per hour. The reservoir above was well washed, filled with ordinary distilled water, covered, and left till next day to acquire the temperature of the room. Then the siphon was inserted, and after the flow had continued half an hour the measurements were begun. The flow continued and the temperature of the air in the closet remained constant at  $22^{\circ}\cdot 2$  C. throughout.

W (grams).	Temperature.	T found.	T at $18^{\circ}$ C.
2.5612	$22^{\circ}\cdot 20$	73.138	73.726
2.5613	$22^{\circ}\cdot 20$	73.141	73.729
2.5615	$22^{\circ}\cdot 15$	73.146	73.727

These measurements were made with a glass frame by the maximum-weight method, and the corresponding values of T found by the formula

$$T = 4.8926 + 14.027w + 7.6891w^2 - 1.0786w^3,$$

which was calculated from a series of measurements of the surface-tension of mixtures of water and alcohol, by two methods, as follows :—

W found (grams).	T by Method A or B (dynes).
1.1033	28.280
1.9180	52.472
2.1220	58.975
2.3261	65.549

A few days later tap-water was allowed to run more slowly through the siphon for four hours, the surface-tension measured in the same way; then a fresh portion allowed to run more rapidly for half an hour, then again for forty-five minutes. The temperature of the air was in each case  $22^{\circ}\cdot 0$  C. The three measurements gave :—

W (grams).	Temperature.	T (dynes).	T at $18^{\circ}$ C.
2.5650	$20^{\circ}\cdot 6$	73.260	73.644
2.5631	$20^{\circ}\cdot 5$	73.190	73.540
2.5613	$20^{\circ}\cdot 5$	73.141	73.491

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# Measuring the Surface-Tension of Liquids.

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In these cases there can be no doubt that the surface was as pure as the interior of the water. Small bits of cork and dust were sprinkled on the surface after the last measurement, as a test, and the surface was swept clean in a few seconds, all visible particles (except the largest) being carried off in the overflow. In finding the maximum weight, in no case was an observation accepted as final when there was the least visible oscillation of the balance or variation of the pointer from zero just before the final overturn.

With the same arrangements for overflow, except that the glass reservoir was replaced by a large galvanized iron tank and that the connecting-tube was in two pieces united by a new perforated cork, a large number of measurements were made by thin plates at various times on tap-water. The highest value in each set of observations is given below. In each case very great care was taken to secure a zero contact-angle.

Plate.	Weight (grm.).	Temperature.	T (dynes).	T at 18° C.
Platinum .....	1.9735	18.95	72.19	72.33
Silver.....	1.1383	19.01	73.22	73.36
Zinc .....	1.8421	19.85	73.29	73.55
Silver.....	1.1358	20.08	73.06	73.35
Platinum .....	1.9904	20.16	72.81	73.12
Glass .....	0.744	20.50	71.91	72.26

These results in connexion with the foregoing point to very distinct differences in the surface-tension of different specimens of water. The very great differences in the values of the temperature-coefficient found by different investigators are probably also due to real differences in the specimens examined. Water free from gases has a temperature-coefficient not far from 0.14 dyne for each degree C. But if care be not taken to free the water from dissolved gases, the coefficient may be as high as 0.20 dyne, or even higher. The great differences in determinations of the critical temperature of water and of alcohol by different observers may be due to the same cause.

My thanks are due to the authorities of Clark University for the facilities afforded me, and to Professor Michelson and Assistant-Professor Webster for valuable suggestions during the progress of this work.

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